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(71)出願人　000005821
松下電器産業株式会社
大阪府門真市大字門真1006番地

(72)発明者　山浦　純一
大阪府門真市大字門真1006番地　松下電器産業株式会社内

(72)発明者　岡村　一広
大阪府門真市大字門真1006番地　松下電器産業株式会社内

(72)発明者　新田　芳明
大阪府門真市大字門真1006番地　松下電器産業株式会社内

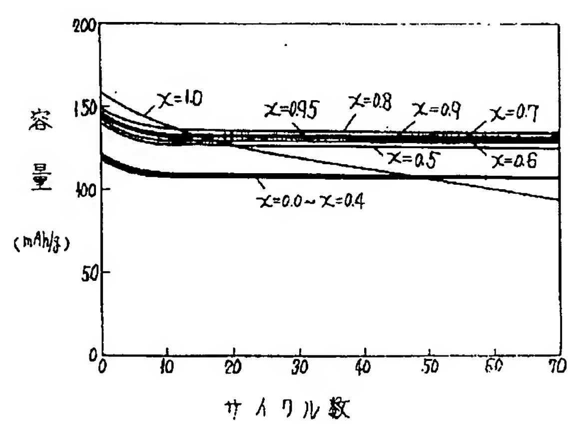
(74)代理人　弁理士　滝本　智之　（外１名）

(54)【発明の名称】　リチウム二次電池用正極活物質の製造法

(57)【要約】

【目的】　Ｎｉの一部をＣｏに確実に置換して一般式$LiNi_xCo_{(1-x)}O_2$で表わされるリチウム含有複合酸化物の結晶構造をほぼ単一相とし、結晶完成度が高く結晶の崩壊がなく結晶内でＬｉが移動し易い安定した結晶場を得ることができる製造法を提供する。

【構成】　ニッケル塩とコバルト塩との混合溶液にアルカリ溶液を加えてニッケルとコバルトの水酸化物を共沈させることによって得たニッケルとコバルトの複合水酸化物を用いてリチウム含有複合酸化物を合成する。



【特許請求の範囲】

【請求項1】　リチウムとニッケルおよびコバルトを含むリチウム含有複合酸化物で、一般式$LiNi_xCo_{(1-x)}O_2$で表わされる式中のx値を$0.95 \geqq x \geqq 0.50$とする正極活物質の製造方法であり、コバルト塩とニッケル塩との混合水溶液にアルカリ溶液を加えてコバルトとニッケルの水酸化物を共沈させることによってコバルトとニッケルの複合水酸化物を得た後、水酸化リチウムなどのリチウム化合物と混合し、この混合物を焼成することを特徴とするリチウム二次電池用正極活物質の製造法。

【請求項2】　コバルトとニッケルの複合水酸化物とリチウム化合物との混合物を、600℃以上800℃以下で焼成する請求項1記載のリチウム二次電池用正極活物質の製造法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明はリチウム二次電池の、とくにその正極活物質の製造法に関するものである。

【0002】

【従来の技術】近年、電子機器のポータブル化、コードレス化が急速に進んでおり、これらの駆動用電源として小形・軽量で、高エネルギー密度を有する二次電池への要望が高い。このような点で非水系二次電池、特にリチウム二次電池はとりわけ高電圧・高エネルギー密度を有する電池として期待が大きい。

【0003】このような中で$LiCoO_2$を正極に、炭素材料を負極に用いた電池が開発されている。$LiCoO_2$の作動電位はLiに対して4Vと高いため電池電圧が高くなるとともに、負極に炭素材を用いてインターカレーション反応を利用しているため金属Liを負極に用いた場合の課題であったデンドライト状Liが負極上に析出することはなく電池の安全性を向上させることができる。

【0004】しかし、Coの資源の問題とコストの問題から、$LiCoO_2$に代わるリチウム含有複合酸化物の開発が進んでおり$LiNiO_2$などが注目されはじめた。$LiNiO_2$ならびに$LiCoO_2$をはじめとするこの種のリチウム含有複合酸化物はいずれも高い電位を示し、かつインターカレーション反応の利用できる同じ六方晶系の結晶構造をもつ層状化合物であるため、正極活物質材料としてその期待が大きい。このような観点から、例えばLi_xNiO_2（米国特許第4302518号）、$Li_yNi_{2-y}O_2$（特開平2－40861号公報）などの$LiNiO_2$に係るもの、あるいは$Li_yNi_xCo_{1-x}O_2$（特開昭63－299056号公報）や$Li_yNi_{1-x}M_xO_2$（但し、MはTi，V，Mn，Feのいずれか）などの$LiNiO_2$のNiの一部を他の金属に置換したリチウム含有複合酸化物が提案されている。その他、$A_xM_yN_zO_2$（但し、Aはアルカリ金属、Mは遷移金属、NはAl，In，Snの一種）（特開昭62－90863号公報）や$Li_xM_yN_zO_2$）（但し、MはFe，Co，Niの中から選ばれた少なくとも一種で、NはTi，V，Cr，Mnの中から選ばれた少なくとも一種）（特開平4－267053号公報）などのリチウム含有複合酸化物も提案されている。そしてこれらの活物質材料を用いて4V級の放電電移をもった高エネルギー密度のリチウム二次電池の開発が進められている。

【0005】

【発明が解決しようとする課題】これらのリチウム含有複合酸化物の中で$LiNiO_2$はリチウムに対し4Vの作動電位を示すので、正極活物質として用いると高エネルギー密度を有する二次電池が実現できる。しかし、電池の充放電サイクルの経過にともなって電池容量が劣化し、50サイクル目では初期容量の65％まで低下し、良好な充放電サイクル特性が得られないという課題があった。

【0006】このような課題に対し、上記に示すようなNiの一部を他の金属に置換したリチウム複合酸化物や多種の金属元素を同時に含むものなどが提案されてきた。しかし、$LiNiO_2$のNiの一部を他の金属に置換したものはサイクル可逆性が向上する一方、放電容量が小さくなり、かつ放電電圧も低くなる傾向にあり、本来要望されている高電圧、高エネルギー密度という特徴を減ずる結果となった。これらの中でNiの一部をCoに置換したものはサイクル可逆性、放電容量、放電電圧のいずれも他のリチウム含有複合酸化物に比べると比較的良好であった。

【0007】ここで、$LiNiO_2$のNiの一部をCoに置換した活物質の合成は、水酸化リチウムなどのLi化合物と水酸化ニッケルなどのNi化合物に水酸化コバルトなどのCo化合物を加えて焼成する方法（以後、複合式合成法と呼ぶ）が一般的であった。Niの一部をCoに置換して結晶構造が単一相である化合物を得るためには焼成温度を600℃～800℃の温度範囲とする。単一相の生成は焼成温度に依存し焼成温度が600℃以下では反応は完結せず単一相を有する化合物は得られない。また、Niの比率が大きくなるほど800℃を超えると単一相にはなるが結晶性は低下する。

【0008】これは、800℃以上の高温で合成すると結晶中でLiの入るべきサイトにNiやCoが入り込んでしまい、結晶構造が乱れることによると考えられる。

【0009】本発明は、このような課題を解決するものであり、Niの一部をCoに確実に置換して一般式$LiNi_xCo_{(1-x)}O_2$で表わされるリチウム含有複合酸化物の結晶構造を単一相とし、結晶完成度が高く結晶の崩壊がなく結晶内でLiが移動し易い安定した結晶場を得ることができる製造法を提供するものである。

【0010】

【課題を解決するための手段】上記課題を解決するため

に、本発明のリチウム二次電池用正極活物質の製造方法は、リチウムとニッケルおよびコバルトを含むリチウム含有複合酸化物で、一般式$LiNi_xCo_{(1-x)}O_2$で表わされ、式中のx値を0．95≧x≧0．70とする正極活物質の製造方法であり、コバルト塩とニッケル塩との混合水溶液にアルカリ溶液を加えてコバルトとニッケルの水酸化物を共沈させることによってコバルトとニッケルの複合水酸化物を得た後、水酸化リチウムなどのリチウム化合物と混合し、この混合物を焼成するものである。

【0011】

【作用】本発明の製造法では、コバルト塩とニッケル塩との混合溶液にアルカリ溶液を加えてコバルトとニッケルの水酸化物を共沈させることによりニッケルとコバルトの複合水酸化物（以下、Ni・Co複合水酸化物）を得ているので、結晶構造がNiの一部をCoで確実に置換した固溶体レベルに至っており、X線回折でも単一相になっていて結晶完成度も極めて高いものとなっている。

【0012】そして、このNi・Co複合水酸化物にLi塩を加えて焼成すると、結晶内でLiが移動し易い結晶構造を有するリチウム含有複合酸化物を得ることができる。さらに本発明では焼成温度を600℃～800℃としているので結晶構造の乱れはない。

【0013】また、NiとCoの混合原子価状態を形成して安定した結晶構造を得るためには、少なくともNiのCoへの置換数は0．05以上必要である。しかし、NiのCoへの置換数が0．5を超えると結晶の歪みの増大や結晶構造の崩れの発生、および混合原子価状態の不釣り合いでLiが動き難い状況を作り出して活物質の容量低下が著しくなる。

【0014】

【実施例】以下、本発明の実施例を図面を参照にしながら説明する。

【0015】まず、本発明のNi・Co複合水酸化物の共沈による製造法を説明する。市販試薬の硫酸ニッケルを水に加え、飽和状態の硫酸ニッケル水溶液を作成し、これに所定量（目的のCo／Ni比に合わせて）の硫酸コバルトを加え、さらに水を加えて調整して硫酸ニッケルおよび硫酸コバルトを含む飽和水溶液を作成した。次いで、撹拌しながらこの水溶液に水酸化ナトリウムを溶解したアルカリ水溶液をゆっくりと加えていくと、NiとCoの水酸化物の沈殿（共沈）が同時に始まった。十分にアルカリ溶液を加えて沈殿が終了したのを見極めた後、濾過して沈殿物を回収し水洗した。pHを測定しながら水洗を繰り返し、残存アルカリがほぼ無くなったのを見極めた後、熱風空気（100℃に設定した熱風乾燥器を用いた）で乾燥させた。

【0016】このようにして得られたNi・Co複合水酸化物のX線回折パターンはきわめて単一相に近いものであり、元素分析の結果、ほぼ目的の比率でCoとNiを含んでいた。

【0017】なお、本実施例では共沈原材料のNi源として硫酸ニッケル、Co源として硫酸コバルトを用いたが、ニッケル源として硝酸ニッケル、コバルト源として硝酸コバルトなど、基本的には水溶液を作りうる塩であればいずれも使用可能である。また、アルカリ溶液としては水酸化ナトリウム水溶液を用いたが、水酸化カリウム水溶液、水酸化リチウム水溶液など他のアルカリ溶液であっても良い。

【0018】次いで、Li化合物との焼成工程を説明する。Li化合物としては水酸化リチウムを用い、上記共沈で得られたNi・Co複合水酸化物にCoとNiの原子数の和とLiの原子数が等量になるように加えてボールミルで粉砕しながら十分混合し、この複合物をアルミナ製るつぼに入れ酸素中において550℃で20時間で1段目の焼成をした後、750℃で2時間で2段目の焼成をした。焼成後室温までゆっくりと冷却し、粉砕したものを正極活物質粉末とした。

【0019】Co／Ni比の異なるいくつかのCo・Ni複合水酸化物について合成を試みた結果、活物質の組成を示す一般式$LiNi_xCo_{(1-x)}O_2$のx値が0．5以上であるとこのリチウム含有複合酸化物のX線回折パターンが単一相で得られた。しかし、x値が0．5未満になるとX線パターンはほぼ単一相ではあるものの、ピーク強度が弱まり結晶性が低下する傾向があった。

【0020】そして、この正極活物質100重量部に対してアセチレンブラックを5重量部加え十分に混合した後、この混合物をN－メチルピロリジノン（NMP）の溶媒に結着剤のポリフッ化ビニリデン（PVDF）を溶解した液で練りペーストとした。なお、PVDFの量は正極活物質100重量部に対して4重量部となるように調整した。次いで、このペーストをアルミ箔の片面に塗着した後、乾燥して圧延し極板とした。図1は本発明の実施例に用いたコイン形リチウム二次電池の縦断面図である。図1において、正極1は前記極板を円板状に打ち抜いたもので、正極ケース2の内側に設置したものである。また、負極3は金属リチウムをステンレス鋼製ネット5上に圧着したもので、封口板4の内側にスポット溶接されている。正極1と負極3の間にはポリプロピレン製セパレータ6が配されており電解液7が注液されている。また、ポリプロピレン製ガスケット8を介して密封した。なお、電解液には1モルの六フッ化リン酸リチウム（$LiPF_6$）を炭酸エチレン（EC）と炭酸ジエチル（DEC）の混合溶媒中に溶かしたものを用いた。

【0021】そして、一般式$LiNi_xCo_{(1-x)}O_2$で表わされる正極活物質のxの値を0，0．1，0．2，0．3，0．4，0．5，0．6，0．7，0．8，0．9，0．95，1．0とし、これらを用いて上記と同様の方法でコイン形電池を作製した。なお、x＝1．

0はＣｏを含まない$LiNiO_2$である。ついで、これらの電池を用いて充放電サイクル寿命試験を行った。充放電条件は、室温（２０℃）で正極に対して０．５ｍＡ／cm^2の定電流で充放電し、充電終止電圧を４．３Ｖ、放電終止電圧を３．０Ｖとして行った。

【００２２】図２は充放電サイクル試験の結果で、ｘ＝０．１～０．４の範囲の正極活物質は初期容量が１２０ｍＡｈ／ｇと小さくなった。

【００２３】ｘ＝０．５～０．９５の範囲の正極活物質は初期容量が１４０～１５０ｍＡｈ／ｇと大きく、かつサイクル劣化も小さく、５０サイクル目で初期容量の９０％を維持しているとともにそれ以後のサイクルの繰り返しにおいても容量低下がほとんど見られなかった。ところが、ｘ＝１．０でＣｏを含まない正極活物質は初期容量こそ１５０ｍＡｈ／ｇ以上のものが得られるもののサイクル劣化は大きく、５０サイクル目で初期容量の６５％まで低下し、その後も劣化が進んだ。

【００２４】以上の結果からも明らかなように、共沈により調整したＮｉ・Ｃｏ複合水酸化物を用いて合成した活物質$LiNi_xCo_{(1-x)}O_2$におけるｘの値は０．５～０．９５の範囲のものが好ましい。

【００２５】次に、一般式$LiNi_xCo_{(1-x)}O_2$で表わされる正極活物質のｘの値が０．０～０．９５の範囲のものについて焼成温度を変える検討を行った。１段目の焼成である５５０℃２０時間の工程は上記と同様に行い、その後の焼成について焼成温度を５５０℃、６００℃、６５０℃、７００℃、７５０℃、８００℃、８５０℃、９００℃とした。そして、これらの正極活物質を用いて上記と同様の電池を構成し、上記と同様の条件の充放電サイクル試験を行った。図３にこの結果を示す。なお、上記式中のｘ値は０．８とした。

【００２６】図３からも明らかなように、焼成温度を６００℃～８００℃として合成した活物質が初期容量、ならびにサイクル特性も良好で、５５０℃のものは初期容量、サイクル性とともに不十分で、８５０℃、９００℃のものは初期容量が若干小さくなり、サイクル劣化も大きくなった。

【００２７】以上の結果より、正極活物質の焼成温度は６００℃～８００℃が良いが、８００℃になるとサイクル劣化が若干大きくなり、初期容量も若干小さめになり、６００℃になると初期容量は良好なもののサイクル劣化が若干大きくなるので、６５０℃～７５０℃が好ましい。

【００２８】本実施例では、ｘ値が０．８の場合のものについて述べたが、ｘ値が０．５０～０．９５の範囲のものについてそれぞれ同様の焼成温度に関する検討を行った結果、ｘ＝０．８の場合と同様の傾向を示す結果が得られた。

【００２９】従来の混合式合成法を用いて、$LiNi_{0.8}Co_{0.2}O_2$の組成を有する正極活物質を合成した。まず、水酸化ニッケルと水酸化リチウムと水酸化コバルトとをＮｉ：Ｃｏ：Ｌｉの原子比が０．８：０．２：１．０となるように秤量し、ボールミルで粉砕しながら混合し、混合物をアルミナるつぼに入れ酸素中において５５０℃、２０時間で１段目の焼成をした後、７５０℃、２時間で２段目の焼成をした。焼成後室温までゆっくりと冷却し、粉砕したものを正極活物質とした。この活物質のＸ線回折パターンは単一相になったが、上記と同様の充放電サイクル試験を行うとサイクル経過にともなう容量低下が大きかった。そこで、$LiNi_xCo_{(1-x)}O_2$におけるｘの値を０，０．１，０．２，０．３，０．４，０．５，０．６，０．７，０．８，０．９として正極活物質を合成し、上記と同様の充放電サイクル試験を行った。この結果を図４に示す。

【００３０】図４に示したように、ｘの値が０．５～０．９の範囲であっても従来の方法により合成した正極活物質ではサイクルの経過に伴う容量低下が本発明のものより大きかった。

【００３１】

【発明の効果】以上のように本発明のリチウム二次電池用正極活物質の製造法では、ニッケル塩とコバルト塩との混合溶液にアルカリ溶液を加えてニッケルとコバルトの水酸化物を共沈させることによりニッケルとコバルトの複合水酸化物を得ているので、結晶構造がＮｉの一部をＣｏで確実に置換した固溶体レベルに至っており、Ｘ線回折でも単一相になっていて結晶完成度が極めて高いものとなっている。そして、このＮｉ・Ｃｏ複合水酸化物にＬｉ塩を加えて焼成すると、結晶内でＬｉが移動し易い結晶構造を有するリチウム含有複合酸化物を得ることができ、容量が大きくサイクル特性に優れた正極活物質を得ることができる。

【図面の簡単な説明】

【図１】本実施例に用いたコイン形リチウム二次電池の断面図

【図２】ｘ値を変化させたときの正極活物質の容量とサイクル数との関係を示す図

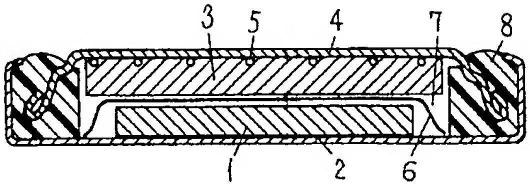
【図３】焼成温度を変化させたときの正極活物質の容量とサイクル数との関係を示す図

【図４】従来の製造法により合成した正極活物質の容量とサイクル数との関係を示す図

【符号の説明】

1　正極
2　正極ケース
3　負極
4　封口板
5　ステンレス鋼製ネット
6　セパレータ
7　電解液
8　ガスケット

【図1】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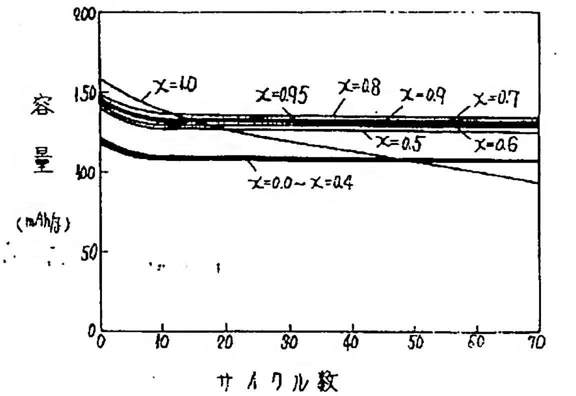
【図2】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(mAh/g)
サイクル数
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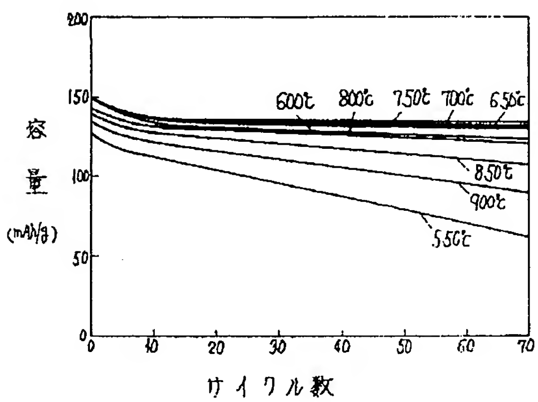
x=0.95
x=0.8
x=0.9
x=0.7
x=0.5
x=0.6
x=0.0～x=0.4

【図3】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(mAh/g)
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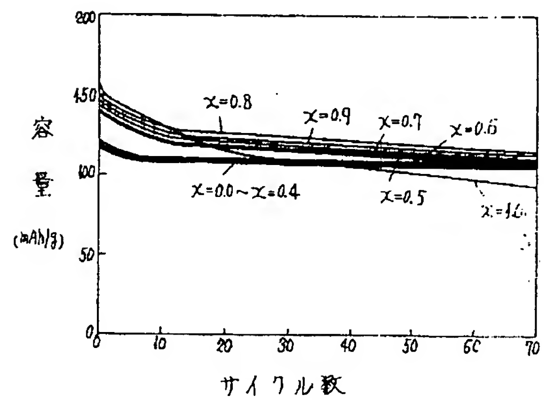
700℃
650℃
850℃
900℃
550℃

【図4】


容量
(mAh/g)
サイクル数
x=0.8
x=0.9
x=0.7
x=0.6
x=0.0～x=0.4
x=0.5

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(71)Applicant : **MATSUSHITA ELECTRIC IND CO LTD**
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(72)Inventor : **YAMAURA JUNICHI**
OKAMURA KAZUHIRO
NITTA YOSHIAKI

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(54) MANUFACTURE OF POSITIVE ELECTRODE ACTIVE MATERIAL FOR LITHIUM SECONDARY BATTERY

(57)Abstract:
PURPOSE: To obtain a positive electrode active material which has a high crystal completing level and an excellent cycle property, by mixing Li compound to Ni-Co compound hydroxide made by adding alkali to the mixing solution of Ni salt and Co salt, and coprecipitating them, and then baking it.
CONSTITUTION: To saturated water solution including Ni salt such as nickel sulfate and Co salt such as cobalt sulfate, alkaline solution such as sodium hydroxide is added, and the hydroxides of Ni and Co are coprecipitated. To the obtained compound hydroxide of Co and Ni, Li compound such as lithium hydroxide is mixed, the resultant compound is baked, and a positive electrode active material shown as LiNixCo(1-x)O2 manufactured. And in the formula, x is made $0.95 \geq x \geq 0$. The baking of the mixture is preferable to carry out at 600 to 800°C. Furthermore, it is cooled slowly to the room temperature after the baking, and then crushed to make a positive electrode active material powder.

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CLAIMS

[Claim(s)]
[Claim 1] With the lithium content multiple oxide containing a lithium, nickel, and cobalt General formula LiNiXCo (1-x) It is the manufacture approach of the positive active material which sets to 0.95>=x>=0.50 x values in the formula expressed with O2. After obtaining the compound hydroxide of cobalt and nickel by adding an alkali solution to the mixed water solution of cobalt salt and nickel salt, and carrying out coprecipitation of the hydroxide of cobalt and nickel, The manufacturing method of the positive active material for lithium secondary batteries characterized by mixing with lithium compounds, such as a lithium hydroxide, and calcinating this mixture.
[Claim 2] The manufacturing method of the positive active material for lithium secondary batteries according to claim 1 which calcinates the mixture of cobalt, the compound hydroxide of nickel, and a lithium compound below 600 degrees C or more 800 degrees C.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention is the thing especially about the manufacturing method of the positive active material of a lithium secondary battery.
[0002]
[Description of the Prior Art] In recent years, portable-izing of electronic equipment and cordless-ization are progressing quickly, it is small and lightweight as these power sources for a drive, and the request to the rechargeable battery which has a high energy consistency is high. A nonaqueous rechargeable battery, especially a lithium secondary battery have great expectation at such a point as a cell which especially has a high voltage and a high energy consistency.
[0003] The cell which thus, used LiCoO2 for the positive electrode and used the carbon material for the negative electrode is developed. 4V, since it is high, while cell voltage becomes high to Li, since the action potential of LiCoO2 used carbon material for the negative electrode and uses the intercalation reaction, the shape of a dendrite Li which was a technical problem at the time of using Metal Li for a negative electrode cannot deposit on a negative electrode, and it can raise the safety of a cell.
[0004] However, development of the lithium content multiple oxide which replaces LiCoO2 is progressing from the problem of the resource of Co, and the problem of cost, and LiNiO2 etc. began to attract attention. Since these kinds including LiNiO2 and LiCoO2 of lithium content multiple oxide [each] is a stratified compound with the crystal structure of the same hexagonal system which shows high potential and can use an intercalation reaction, that expectation is great as a positive-active-material ingredient. The lithium content multiple oxide which permuted some nickel of LiNiO(s)2, such as a

thing which starts $LiNiO(s)2$, such as $LiXNiO2$ (U.S. Pat. No. 4302518) and $LiyNi2-yO2$ (JP,2-40861,A), for example, or $LiyNiXCo1-XO2$ (JP,63-299056,A), $LiyNi1-XMXO2$ (however, M Ti, V, Mn, or Fe), by other metals from such a viewpoint is proposed. In addition, lithium content multiple oxides, such as $AxMyNZO2$ (however, A alkali metal and M transition metals and N a kind of aluminum, In, and Sn) (JP,62-90863,A) and $LiXMyNZO2$ (however, M was chosen from Fe, Co, and nickel it is a kind at least and N was chosen from Ti, V, Cr, and Mn at least a kind) (JP,4-267053,A), are also proposed. And development of the lithium secondary battery of the high energy consistency which had 4V class discharge **** using these active material ingredients is furthered.
[0005]
[Problem(s) to be Solved by the Invention] Since $LiNiO2$ shows the action potential of 4V to a lithium in these lithium content multiple oxides, if it uses as positive active material, the rechargeable battery which has a high energy consistency is realizable. However, cell capacity deteriorated with progress of the charge-and-discharge cycle of a cell, by 50 cycle eye, it fell to 65% of initial capacity, and the technical problem that a good charge-and-discharge cycle property was not acquired occurred.
[0006] What contains in coincidence the metallic element of the lithium multiple oxide and variety which permuted some nickel as shown above by other metals has been proposed to such a technical problem. However, while cycle reversibility of what permuted some nickel of $LiNiO2$ by other metals improved, it is in the inclination for discharge capacity to become small and for discharge voltage to also become low, and resulted in reducing the description of the high voltage and high energy consistency which are originally demanded. Both cycle reversibility discharge capacity and the discharge voltage of what permuted some nickel by Co in these were comparatively good compared with other lithium content multiple oxides.
[0007] Here, composition of the active material which permuted some nickel of $LiNiO2$ by Co had the common method (it is henceforth called a compound expression synthesis method) of adding and calcinating Co compounds, such as cobalt hydroxide, to Li compounds, such as a lithium hydroxide, and nickel compounds, such as nickel hydroxide. In order to permute some nickel by Co and to obtain the compound whose crystal structure is a single phase, let burning temperature be a 600 degrees C - 800 degrees C temperature requirement. The compound with which burning temperature does not complete generation of a single phase below 600 degrees C depending on burning temperature, but a reaction has a single phase is not obtained. Moreover, if it exceeds 800 degrees C so that the ratio of nickel becomes large, although it will become a single phase, crystallinity falls.
[0008] If it compounds at an elevated temperature 800 degrees C or more, nickel and Co will enter the site into which Li should go in a crystal, and this is considered to be because for the crystal structure to be confused.
[0009] This invention offers the manufacturing method which can obtain the stable crystal field where such a technical problem is solved, the crystal structure of a lithium content multiple oxide which permutes some nickel by Co certainly and is expressed with general formula $LiNiXCo(1-X)\ O2$ is made into a single phase, there is no collapse of a crystal highly [crystal completeness], and Li tends to move within a crystal.
[0010]
[Means for Solving the Problem] In order to solve the above-mentioned technical

problem, the manufacture approach of the positive active material for lithium secondary batteries of this invention With the lithium content multiple oxide containing a lithium, nickel, and cobalt General formula LiNiXCo (1-X) It is the manufacture approach of the positive active material which is expressed with O2 and sets x values in a formula to 0.95>=x>=0.70. After obtaining the compound hydroxide of cobalt and nickel by adding an alkali solution to the mixed water solution of cobalt salt and nickel salt, and carrying out coprecipitation of the hydroxide of cobalt and nickel, it mixes with lithium compounds, such as a lithium hydroxide, and this mixture is calcinated.

[0011]

[Function] According to the manufacturing method of this invention, since the compound hydroxide (following and nickel-Co compound hydroxide) of nickel and cobalt has been obtained by adding an alkali solution to the mixed solution of cobalt salt and nickel salt, and carrying out coprecipitation of the hydroxide of cobalt and nickel, it has resulted in the solid-solution level which permuted some nickel certainly by Co, and also by the X diffraction, the crystal structure has a single phase and has become what has very high crystal completeness.

[0012] And if Li salt is added and calcinated to this nickel-Co compound hydroxide, the lithium content multiple oxide which has the crystal structure which Li tends to move within a crystal can be obtained. Since burning temperature is furthermore made into 600 degrees C - 800 degrees C by this invention, there is no turbulence of the crystal structure.

[0013] Moreover, in order to acquire the crystal structure which formed the mixed valence condition of nickel and Co and was stabilized, the number of permutations to Co of nickel at least is [0.05 or more] required. However, if the number of permutations to Co of nickel exceeds 0.5, increase of distortion of a crystal, generating of collapse of the crystal structure, and a mixed valence condition are disproportionate, the situation of being hard to move Li will be made and capacity deterioration of an active material will become remarkable.

[0014]

[Example] Hereafter, the example of this invention is explained for a drawing, making it reference.

[0015] First, the manufacturing method by the coprecipitation of the nickel-Co compound hydroxide of this invention is explained. The nickel sulfate of a commercial reagent was added to water, the nickel-sulfate water solution of a saturation state was created, the cobalt sulfate of the specified quantity (doubling with the target Co/nickel ratio) was added to this, and the saturated water solution which adds and adjusts water further and contains a nickel sulfate and cobalt sulfate was created. Subsequently, when the alkali water solution which dissolved the sodium hydroxide in this water solution was added slowly, stirring, precipitate (coprecipitation) of the hydroxide of nickel and Co started in coincidence. It filtered, and precipitate was collected and rinsed, after having discerned that fully added the alkali solution and precipitate was completed. Rinsing is repeated measuring pH, and after discerning that residual alkali was lost mostly, it was made to dry with hot blast air (for the air forced oven set as 100 degrees C to have been used).

[0016] Thus, the X diffraction pattern of the obtained nickel-Co compound hydroxide was very close to the single phase, and contained Co and nickel by the target ratio mostly as a result of elemental analysis.

[0017] In addition, although cobalt sulfate was used as a nickel sulfate and a source of Co as a source of nickel of a coprecipitation raw material in this example, all are usable if a cobalt nitrate etc. is the salt which can make a water solution fundamentally as nickel nitrate and a source of cobalt as a source of nickel. Moreover, although the sodium-hydroxide water solution was used as an alkali solution, you may be other alkali solutions, such as a potassium-hydroxide water solution and a lithium-hydroxide water solution.

[0018] Subsequently, a baking process with Li compound is explained. The 2nd step of baking was carried out at 750 degrees C in 2 hours after [while the ball mill ground in addition so that the sum of the atomic number of Co and nickel and the atomic number of Li might become the nickel-Co compound hydroxide obtained by the above-mentioned coprecipitation ana, using a lithium hydroxide as a Li compound,] mixing enough, putting this composite into the crucible made from an alumina and carrying out the 1st step of baking at 550 degrees C into oxygen in 20 hours. It cooled slowly to the after [baking] room temperature, and what was ground was used as positive-active-material powder.

[0019] As a result of trying composition about some Co-nickel compound hydroxides with which Co/nickel ratios differ, the X diffraction pattern of this lithium content multiple oxide was obtained with the single phase as x values of general formula LiNiXCo(1-X) O2 which show the presentation of an active material are 0.5 or more. However, although the X-ray pattern was a single phase mostly when x values became less than 0.5, there was an inclination for peak intensity to become weaker and for crystallinity to fall.

[0020] And after mixing acetylene black to this positive-active-material 100 weight section in 5 weight ****** 10 minutes, this mixture was scoured with the liquid which dissolved the polyvinylidene fluoride (PVDF) of a binder in the solvent of N-methyl pyrrolidinone (NMP), and it considered as the paste. In addition, the amount of PVDF was adjusted so that it might become 4 weight sections to the positive-active-material 100 weight section. Subsequently, after plastering one side of aluminum foil with this paste, it dried and rolled out and considered as the plate. Drawing 1 is drawing of longitudinal section of the coin form lithium secondary battery used for the example of this invention. In drawing 1 , a positive electrode 1 is what pierced said plate to disc-like, and is installed inside the positive-electrode case 2. Moreover, a negative electrode 3 is what stuck the metal lithium by pressure on the network 5 made from stainless steel, and spot welding is carried out inside the obturation plate 4. The separator 6 made from polypropylene is allotted between the positive electrode 1 and the negative electrode 3, and the electrolytic solution 7 is poured in. Moreover, it sealed through the gasket 8 made from polypropylene. In addition, what melted the one-mol 6 phosphorus-fluoride acid lithium (LiPF6) in ethylene carbonate (EC) and the mixed solvent of diethyl carbonate (DEC) was used for the electrolytic solution.

[0021] and the value of x of positive active material expressed with general formula LiNiXCo(1-X) O2 -- 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 0. -- it was referred to as 95 and 1.0 and the coin form cell was produced by the same approach as the above using these. In addition, x= 1.0 is LiNiO2 which does not contain Co. Subsequently, charge-and-discharge cycle life test was performed using these cells. The charge and discharge of the charge-and-discharge conditions were carried out according to the

constant current of 0.5 mA/cm2 to the positive electrode at the room temperature (20 degrees C), and they performed 4.3V and discharge final voltage for the charge termination electrical potential difference as 3.0V.

[0022] As for drawing 2 , by the result of a charge-and-discharge cycle trial, the positive active material of the range of x=0.1-0.4 became [initial capacity] as small as 120 mAh/g.

[0023] While the positive active material of the range of x=0.5-0.95 had an initial capacity as large as 140 - 150 mAh/g, and cycle degradation was also small and maintaining 90% of initial capacity by 50 cycle eye, also in the repeat of the cycle after it, a capacity fall was hardly seen. However, although, as for the positive active material which does not contain Co by x= 1.0, the thing of 150 or more mAh/g was obtained just for initial capacity, cycle degradation was large, it fell to 65% of initial capacity by 50 cycle eye, and, also after that, degradation progressed.

[0024] The value of x in active material $LiNiXCo(1-x) O2$ compounded using the nickel-Co compound hydroxide adjusted according to coprecipitation has the desirable thing of the range of 0.5-0.95 so that clearly also from the above result.

[0025] Next, the value of x of positive active material expressed with general formula $LiNiXCo(1-X) O2$ performed examination which changes burning temperature about the thing of the range of 0.0-0.95. 550-degree-C process of 20 hours which is the 1st step of baking was performed like the above, and made burning temperature 550 degrees C, 600 degrees C, 650 degrees C, 700 degrees C, 750 degrees C, 800 degrees C, 850 degrees C, and 900 degrees C about subsequent baking. And the same cell as the above was constituted using such positive active material, and the charge-and-discharge cycle trial of the same conditions as the above was performed. This result is shown in drawing 3 . In addition, x values in the above-mentioned formula were set to 0.8.

[0026] The initial capacity and cycle property also had the good active material which compounded burning temperature as 600 degrees C - 800 degrees C so that clearly also from drawing 3 , the 550-degree C thing was inadequate in initial capacity and cycle nature, as for the thing (850 degrees C and 900 degrees C), initial capacity became a little and small, and cycle degradation also became large.

[0027] Since cycle degradation of what has a good initial capacity will become a little and large if cycle degradation will become a little and large if it becomes 800 degrees C, although the burning temperature of positive active material has 600 degrees C - 800 degrees C better than the above result, initial capacity also becomes a little and more smallish and it becomes 600 degrees C, 650 degrees C - 750 degrees C are desirable.

[0028] Although this example described the thing in case x values are 0.8, as a result of x values' performing examination about the burning temperature respectively same about the thing of the range of 0.50-0.95, the result which shows the same inclination as the case of x= 0.8 was obtained.

[0029] The positive active material which has the presentation of $LiNi0.8Co\ 0.2O2$ was compounded using the conventional mixed formula synthesis method. First, the 2nd step of baking was carried out in 750 degrees C and 2 hours after having carried out weighing capacity of nickel hydroxide, a lithium hydroxide, and the cobalt hydroxide so that the atomic ratio of nickel:Co:Li might be set to 0.8:0.2:1.0, it mixed while the ball mill ground, and putting mixture into the alumina crucible and carrying out the 1st step of baking into oxygen in 550 degrees C and 20 hours. It cooled slowly to the after [baking]

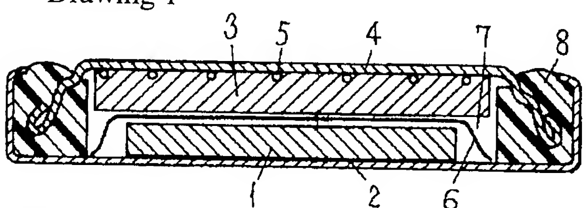
room temperature, and what was ground was used as positive active material. Although the X diffraction pattern of this active material became a single phase, when the same charge-and-discharge cycle trial as the above was performed, the capacity fall accompanying cycle progress was large. then, the value of x in $LiNi_XCo_{(1-X)}O_2$ -- 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0. -- positive active material was compounded as 8 and 0.9, and the same charge-and-discharge cycle trial as the above was performed. This result is shown in drawing 4 .

[0030] As shown in drawing 4 , even if the range of the value of x was 0.5-0.9, the capacity fall accompanying progress of a cycle with the positive active material compounded by the conventional approach was larger than the thing of this invention.

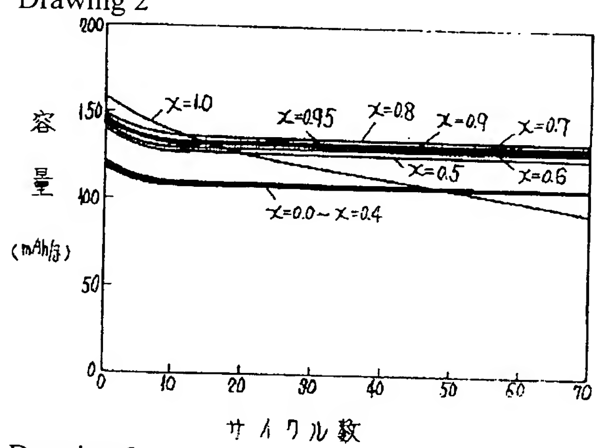
[0031]

[Effect of the Invention] As mentioned above, by the manufacturing method of the positive active material for lithium secondary batteries of this invention, since the compound hydroxide of nickel and cobalt has been obtained by adding an alkali solution to the mixed solution of nickel salt and cobalt salt, and carrying out coprecipitation of the hydroxide of nickel and cobalt, the crystal structure has resulted in the solid-solution level which permuted some nickel certainly by Co, has a single phase also by the X diffraction, and it has become what has very high crystal completeness. And if Li salt is added and calcinated to this nickel-Co compound hydroxide, the lithium content multiple oxide which has the crystal structure which Li tends to move within a crystal can be obtained, and the positive active material capacity excelled [positive active material] in the cycle property greatly can be obtained.

Drawing 1



Drawing 2



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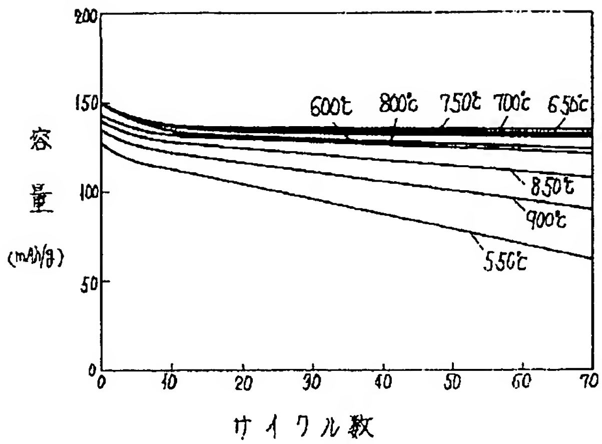

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(mAh/g)
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20
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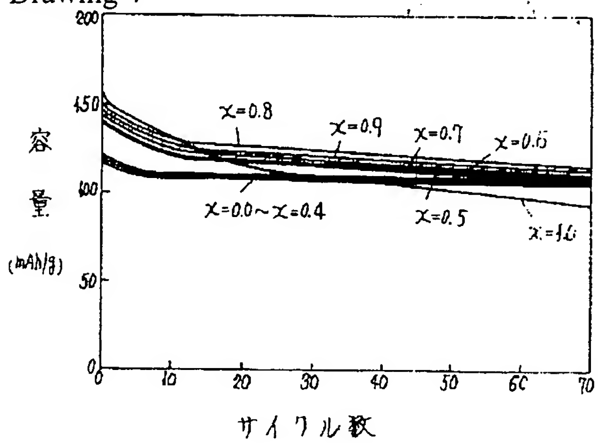
60
70
サイクル数

Drawing 4



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60
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サイクル数